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Synthesis and Structures of Infinite Sheet Copper(I) Complex Polymers with 2,6-Dimethylpyrazine, $\{[Cu_2(C_6H_8N_2)_3](ClO_4)_2(C_3H_6O)_2\}_\infty$, and with 2-Chloropyrazine, $\{[Cu_2(C_4H_3N_2Cl)_{4.5}](ClO_4)_2\}_\infty$[#]

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The new copper(I) coordination polymers, $\{[Cu_2(2,6\text{-}Me_2pz)_3](ClO_4)_2(C_3H_6O)_2\}_\infty$ (**1**) and $\{[Cu_2(2\text{-}Clpz)_{4.5}](ClO_4)_2\}_\infty$ (**2**) (2,6-Me_2pz=2,6-dimethylpyrazine; 2-Clpz=2-chloropyrazine) have been synthesized and their structures have been X-ray crystallographically characterized. **1** crystallizes in the monoclinic, space group $P2_1/a$ with a=15.520(5), b=19.315(2), c=12.493(2) Å, β=110.82(2)°, U=3322(2) Å^3, and Z=4. **2** is orthorhombic, space group $Pbca$ with a=28.567(6), b=17.560(9), c=11.512(9) Å, U=5774(8) Å^3, and Z=8. These complexes show an infinite sheet structure of macrocations with uninteracting ClO_4^- anion. **1** shows planar sheets composed of Cu_6 hexagons, in which copper atoms are three-coordinate and linked by 2,6-Me_2pz molecules. Acetone molecules sit over the cavities of the Cu_6 hexagons, resulting in an intercalated layer between the copper sheets. **2** provides the unique polymers having an unprecedented four coordination geometry in binary copper–pyrazine systems. There are terminal and bridging types of 2-Clpz molecules, which produce Cu_6 and Cu_4 motifs for infinite pleated sheets. The factors governing the mode of polymerization are found by examination of the crystal structures for a series of copper(I) polymers of pyrazine derivatives.

The infinite chain and sheet structure of metal complexes are of substantial interest in understanding the solid state chemistry of metal complexes. Crystalline polymers having copper complex units provide not only novel structures and geometries,[1)] but also interesting properties.[2—5)] However, on the synthetic point of view, there are sparse literatures, which have elucidated the relationship between the polymer and monomer structures, toward rational synthesis of copper complex polymers in the single crystal phase. One field of this synthetic chemistry concerns the choice of linking ligands. Inorganic ligands such as halide ions are used for complexes known for three decades,[1)] while the polymer compounds having organic ligands are still sparse.

Pyrazine (pz) acts as a linking ligand, especially in low-dimensional compounds, and many infinite chain copper(II) compounds have been synthesized.[6—12)] Very recently, several copper(I) coordination polymers have been isolated and characterized by X-ray crystallography. Interestingly, the geometries of the copper atoms and the dimensionality of polymer modes are influenced by the substituents on pyrazine. Tetramethylpyrazine (Me_4pz) provides a linear chain structure,[13)] while two-dimensional structure is built from hexagonal motifs of $Cu_6(2,3\text{-}Me_2pz)_6$ (2,3-Me_2pz=2,3-dimethylpyrazine).[14)] The similar hexagonal motif is also obtained by use of pyrazine and CH_3CN.[13)] The two-dimensional structure is described as pleated sheets, which come from a chair-like Cu_6 motif. The first question arises: is it possible to provide the complete planar sheets of flat Cu_6 motifs? The second one is whether there are two-dimensional structures comprising of motifs other than Cu_6 ones or not. The objectives in this work are to answer these questions, and thus, to build up new structure of copper(I) polymer compounds containing pyrazines. This work concerns with the discovery and the sturctural characterization of new two-dimensional copper(I) polymers, whose structures are controlled by the modification of linking liqands.

Experimental

All operations were carried out under an atmosphere of purified argon. Solvents were dried by conventional methods and distilled under argon. $[Cu(C_2H_4)ClO_4]$ was obtained from the reduction of $Cu(ClO_4)_2\cdot 6H_2O$ by copper wire, whose preparation has mentioned previously.[15)] 2,6-Dimethylpyrazine (2,6-Me_2pz) and 2-chloropyrazine (2-Clpz) were purchased from Aldrich Chemicals.

Preparation of $\{[Cu_2(C_6H_8N_2)_3](ClO_4)_2(C_3H_6O)_2\}_\infty$ (1). An acetone (3 mL) solution of Me_2pz (0.45 mmol) was added to an acetone (3 mL) solution of $[Cu(C_2H_4)ClO_4]$ (0.1 mmol), and stirred for 15 min under ethylene to give the colorless solution. Ethylene atmosphere was replaced with argon atmosphere. The reaction solution was filtered and the resultant colorless filtrate was sealed in a glass tube. Within 2 d stable yellow plate crystals were obtained at 25 °C (yield 46.9%).

Preparation of $\{[Cu_2(C_4H_3N_2Cl)_{4.5}](ClO_4)_2\}_\infty$ (2). The orange brick crystals of **2** were obtained in a similar way.

Crystallography. Crystal Data. $Cu_2Cl_2O_{10}N_6C_{24}H_{36}$, monoclinic, space group $P2_1/a$, a=15.520(5), b=19.315(2), c=12.493(2) Å, β=110.82(2)°, U=3322(2) Å^3, Z=4, D_c=1.533 g cm^{-3}, $F(000)$=1576, λ(Mo $K\alpha$)=0.71069 Å, μ=15.02 cm^{-1}, T=23 °C. Specimen size, 0.25×0.25×0.1 mm, $2\theta_{max}$=55.0°, N, N_o=7880, 4059, R, R_w=0.078, 0.118.

$Cu_2Cl_{6.5}O_8N_9C_{18}H_{13}$, orthorhombic, space group $Pbca$, a=28.567(6), b=17.560(9), c=11.512(9) Å, U=5774(8) Å^3, Z=8, D_c=1.934 g cm^{-3}, $F(000)$=3332, λ(Mo $K\alpha$)=0.71069 Å, μ=21.44 cm^{-1}, T=23 °C. Specimen size,

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[#] This paper is dedicated to the late Professor Hiroshi Kato.

0.30×0.30×0.40 mm, $2\theta_{\max}=55.2^\circ$, N, $N_o=7652$, 2164, R, $R_w=0.066$, 0.069.

X-Ray Data Collection. General crystallographic data and procedures for this paper are as follows. As a general rule, crystals were glued on top of a glass fiber. For each compound unit cell constants were determined from the geometric parameters of 20 well-centered reflections with 2θ values in the range of $20^\circ<2\theta<32^\circ$. Then, unique data set was measured to a 2θ limit predetermined from the scope of the data, using a Rigaku RASA5R automated diffractometer fitted with a monochromatic Mo $K\alpha$ radiation source ($\lambda=0.71073$ Å) and operating in conventional ω–2θ scan mode at 23 °C. N Independent reflections were obtained, N_o with $F_o>3\sigma(F_o)$ being considered "observed" and used in the full-matrix least-squares refinements. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorenz and polarization effects.

Solution and Refinement of the Structures of 1 and 2. The structure was solved by MITHRIL,[16] and refined by full-matrix least squares, anisotropically for all non-hydrogen atoms. All the hydrogen atoms were located in a difference Fourier map and introduced as fixed contributors in the final stage of the refinement. Residuals at convergence are quoted on $|F|$: $R=\sum||F_o|-|F_c||/\sum|F_o|$ and $R'=[(\sum w(|F_o|-|F_c|)^2/\sum wF_o^2)]^{1/2}$.

In the case of **2** one of 2-Clpz molecules sits on the crystallographic inversion center, indicating that the pyrazine molecule has two chlorine atoms. The used ligand for this synthesis is pure 2-Clpz and there are no possibilities to contain 2,5-Cl_2pz. Thus, the Cl(3) atom for this ligand is disordered with the site occupancies of 0.5. This treatment is verified to be correct by its stable refinement.

The final positional parameters are given in Tables 1 and 2.[17]

Table 1. Fractional Coordinates for $\{[Cu_2(Me_2pz)_3](ClO_4)_2\cdot 2(Me_2CO)\}_\infty$

Atom	x	y	z	B_{eq}
Cu(1)	0.2007(1)	0.06555(7)	0.2838(1)	3.24(6)
Cu(2)	0.2342(1)	−0.09595(7)	−0.2000(1)	3.43(6)
Cl(1)	0.4860(3)	0.1645(2)	0.2547(4)	5.5(2)
Cl(2)	0.0253(3)	0.1121(2)	0.7767(3)	5.3(2)
O(1)	0.5241(9)	0.1188(6)	0.189(1)	8.4(7)
O(2)	0.455(1)	0.1263(7)	0.332(1)	10.7(9)
O(3)	0.554(1)	0.2076(9)	0.320(2)	15(1)
O(4)	0.411(1)	0.1990(8)	0.175(1)	13(1)
O(5)	0.013(1)	0.041(1)	0.768(2)	14(1)
O(6)	0.019(2)	0.140(1)	0.872(2)	19(2)
O(7)	0.098(2)	0.133(1)	0.755(3)	29(3)
O(8)	−0.036(3)	0.133(2)	0.697(2)	39(4)
O(9)	0.368(1)	0.1135(7)	0.625(1)	11.7(9)
O(10)	0.736(1)	0.1653(7)	0.812(1)	9.3(8)
N(1)	0.1995(7)	0.0201(5)	0.1326(8)	3.3(4)
N(2)	0.2165(6)	−0.0468(4)	−0.0651(7)	2.8(4)
N(3)	0.2136(6)	0.0236(4)	0.4385(7)	2.6(4)
N(4)	0.2307(7)	−0.0408(4)	0.6537(8)	3.3(4)
N(5)	0.2109(6)	0.1673(5)	0.2587(8)	3.2(4)
N(6)	0.2469(6)	0.3043(4)	0.2213(7)	2.6(4)
C(1)	0.1416(8)	−0.0273(6)	0.074(1)	3.0(5)
C(2)	0.1482(8)	−0.0624(6)	−0.027(1)	3.2(5)
C(3)	0.2757(8)	0.0043(6)	−0.007(1)	3.2(5)
C(4)	0.2658(9)	0.0373(6)	0.091(1)	3.5(5)
C(5)	0.081(1)	−0.1156(7)	−0.088(1)	5.3(7)
C(6)	0.350(1)	0.0232(7)	−0.053(1)	4.9(7)
C(7)	0.1548(8)	0.0397(5)	0.4950(9)	2.6(4)
C(8)	0.1661(9)	0.0087(6)	0.605(1)	3.7(5)
C(9)	0.2897(9)	−0.0525(6)	0.597(1)	3.7(5)
C(10)	0.2823(8)	−0.0215(6)	0.490(1)	3.3(5)
C(11)	0.079(1)	0.0878(8)	0.440(1)	5.6(7)
C(12)	0.351(1)	−0.0333(7)	0.431(1)	4.9(6)
C(13)	0.1652(8)	0.1984(6)	0.157(1)	3.4(5)
C(14)	0.1813(8)	0.2676(6)	0.1352(9)	2.8(4)
C(15)	0.2955(8)	0.2709(6)	0.323(1)	3.4(5)
C(16)	0.2749(9)	0.2034(6)	0.343(1)	3.5(5)
C(17)	0.126(1)	0.3030(7)	0.020(1)	5.0(6)
C(18)	0.375(1)	0.3075(6)	0.414(1)	5.5(6)
C(19)	0.451(1)	0.1179(8)	0.682(2)	6.1(8)
C(20)	0.502(1)	0.178(1)	0.665(2)	10(1)
C(21)	0.501(1)	0.060(1)	0.763(2)	8(1)
C(22)	0.757(1)	0.21	0.774(2)	7(1)
C(23)	0.807(2)	0.275(1)	0.861(2)	14(2)
C(24)	0.734(2)	0.236(1)	0.649(2)	14(2)

Results and Discussion

Description of the Structure 1. Figure 1(a) and (b) show one of asymmetric units around the respective copper atoms of **1**. The units are repeated and jointed by copper(I)–pyrazine coordination bonds to give the cationic infinite two-dimensional sheets, which spread out along the bc plane. A schematic drawing of Cu_6 motifs shows planar hexagons (Fig. 1(c) and (d)). The Cu(1) and Cu(2) atoms have Y-shaped form with three nitrogen atoms but the environment is different because of the two nonidentical nitrogen donors of 2,6-Me_2pz. The Cu(1) has a N_2N^* environment while the Cu(2) NN^*_2 when the nitrogen atom close to the neighboring methyl groups is denoted as N*. The Cu_6 motif is constructed by the alternating arrangement of the two different copper moieties. Unexpectedly, all the Cu–N bond distances for Cu(1) and Cu(2) (1.950(8)—2.019(8) Å) are equal within 0.05 Å, close to those of typical three-coordinate 2-picoline complex, $[Cu(2\text{-}pc)_3]ClO_4$ (1.97—2.02 Å).[18] The N–Cu–N angles in each copper are different and ranges from ca. 110° to ca. 130°, making the geometry asymmetric. This asymmetry is attributed to the steric effect of N* sites; there are apparent correlation of the spatial arrangement of N and N* atoms with the angles. However, the subsituents exert no direct effects on the coordination number. This is due to the coordination number lower than four. The Cu_6 motif is not perfect hexagon and distorted just like as compressed from the two directions shown by the arrows in Fig. 1(d). These structural characteristics make this copper complex polymer quite unique.

The distances between the two copper atoms linked by a 2,6-Me_2pz range from 6.710(2) to 6.743(2) Å. The two mutually-confronted pyrazines on the sides of the hexagon are sitting out of the plane and parallel to each other, providing a large cavity of hexanuclear copper atoms. As in Fig. 1(c) acetone molecules

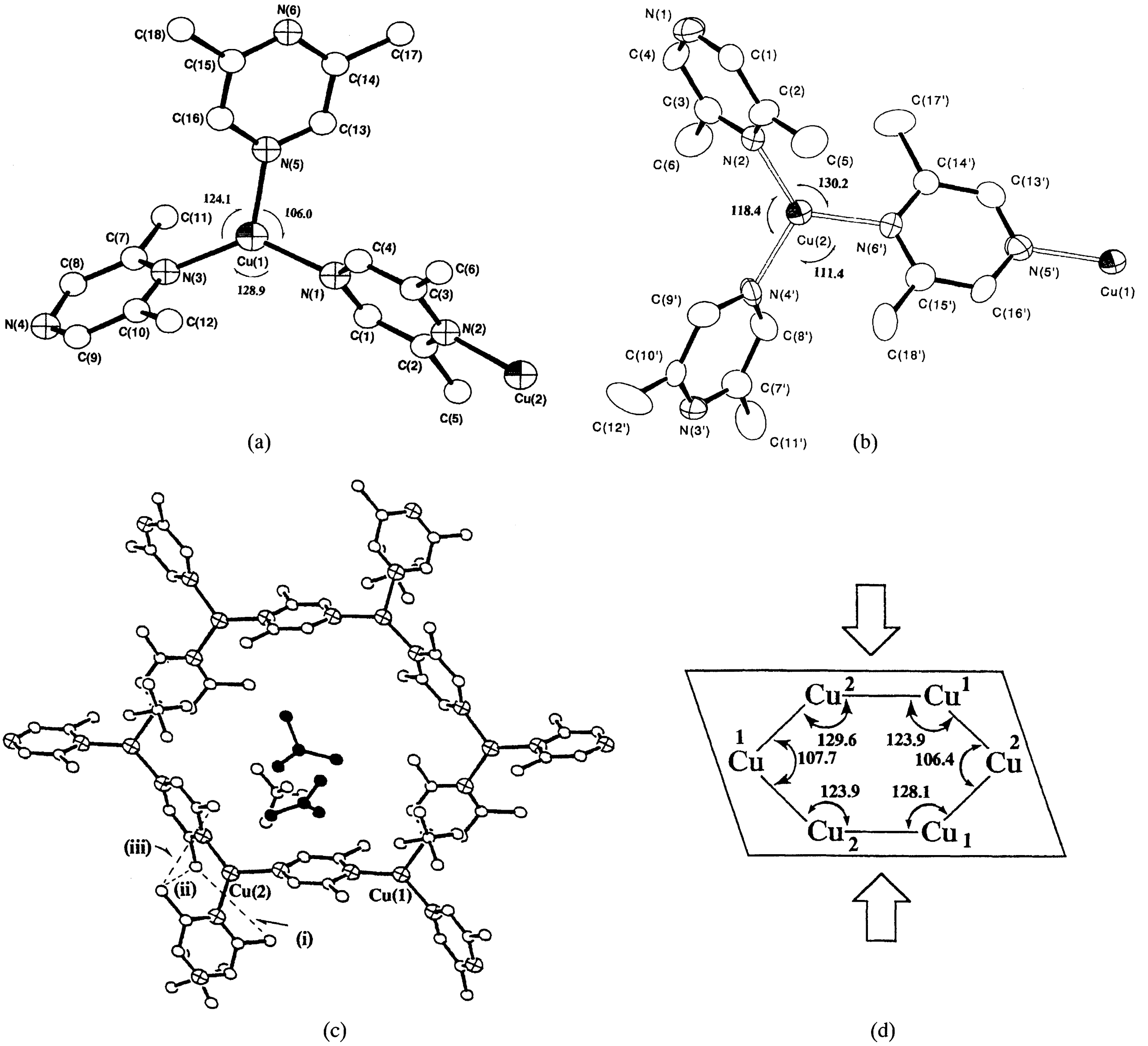

Fig. 1. ORTEP views of portions of $[Cu_2(2,6\text{-}Me_2pz)_3](ClO_4)_2{\cdot}2(Me_2CO)]_\infty$. Geometries of copper(1) (a) and copper(2) (b) as asymmetric units. (c) Hexagonal motif of $Cu_6(2,6\text{-}Me_2pz)_6$, perchlorate anions and acetone molecules. The crystal structure is projected down the *b* axis. The carbon and oxygen atoms of acetone molecules are denotes as shaded circles. The dashed lines denote the main contact of the methyl groups of the neighbored ligands. The distances between carbon atoms are (i) C(5)···C(18)=4.42(2) Å, (ii) C(5)···C(17)=4.60(2) Å and (iii) C(6)···C(17)=4.28(2) Å. (d) Schematic structure of a copper hexagon. The angles in (d) are not the N–Cu–N angles but those between the Cu–Cu vectors.

are not included in cavities but placed over cavities, dissimilar to the case of $\{[Cu(pz)_{3/2}(CH_3CN)](PF_6){\cdot}0.5C_3H_6O\}_\infty$,[13] while the counter anions, ClO_4^-, are placed above the sides. Thus the crystal structure is described as alternation of acetone-perchlorate layers and flat copper(I) polymer layers. The distance between the neighboring copper layers is ca. 6.5 Å, which is that between the two copper atoms (Tables 3 and 4).

Description of the Structure 2. Figure 2(a) shows an asymmetric unit of complex **2**. There are two tetrahedral copper moieties. The bond distances and angles for the copper(2) are very close to those of a typical $[Cu(pyridine)_4]^+$ (Cu–N=2.05 Å, and 110 — 111°),[19] indicative of a regular tetrahedron. On the other hand, the Cu(1) moiety has two extremes for the Cu–N and N–Cu–N values, showing a distorted tetrahedron: The two short and long average distances are 2.02(1) and 2.14(1) Å, respectively, and the small angles range from 97.2(4) to 99.1(4)° (average 98.4(4)°) and the large angles range from 110.8(4) to 126.3(5)° (average 119.4(5)°). The coordination sphere of the copper atoms are denoted as $Cu(1)N^*{}_3N$ and $Cu(2)N^*N_3$, where N* is one close to Cl atom. On this basis both copper atoms are not the type of $CuN^*{}_4$.

Table 2. Positional Parameters and B_{eq} for $\{[Cu_2(2\text{-}Clpz)_{4.5}](ClO_4)_2\}_\infty$

Atom	x	y	z	B_{eq}
Cu(1)	0.57288(6)	0.1395(1)	0.0987(1)	2.87(8)
Cu(2)	0.81595(6)	0.1488(1)	0.1252(1)	2.72(8)
Cl(1)	0.6431(1)	−0.0085(2)	0.1837(4)	3.9(2)
Cl(2)	0.5208(2)	0.0887(2)	0.3454(4)	5.1(2)
Cl(3)[a)]	0.4600(3)	0.1459(4)	0.1012(7)	4.1(4)
Cl(4)	0.8214(2)	−0.1392(2)	−0.0908(3)	4.6(2)
Cl(5)	0.8049(2)	0.0672(2)	0.3817(3)	4.0(2)
Cl(6)	0.2276(1)	0.1336(2)	0.7257(3)	2.93(7)
Cl(7)	0.4642(2)	0.1313(3)	0.7284(4)	4.7(1)
O(1)	0.2494(5)	0.0859(7)	0.642(1)	7.4(3)
O(2)	0.2473(5)	0.1198(7)	0.837(1)	6.7(3)
O(3)	0.4294(5)	0.1363(8)	0.814(1)	8.9(4)
O(4)	0.5024(4)	0.0849(7)	0.773(1)	6.6(3)
O(5)	0.4778(5)	0.2032(9)	0.697(1)	9.9(4)
O(6)	0.4430(6)	0.095(1)	0.635(2)	12.5(6)
O(7)	0.2350(4)	0.2107(6)	0.691(1)	6.2(3)
O(8)	0.1811(5)	0.1143(8)	0.732(1)	8.5(4)
N(1)	0.6475(4)	0.1269(6)	0.095(1)	2.3(5)
N(2)	0.7446(4)	0.1357(6)	0.120(1)	2.7(5)
N(3)	0.5669(4)	0.1991(6)	0.248(1)	2.5(6)
N(4)	0.5669(4)	0.2874(6)	0.452(1)	2.3(6)
N(5)	0.5306(4)	0.0546(6)	0.046(1)	2.7(6)
N(6)	0.8473(4)	0.0476(6)	0.082(1)	2.5(6)
N(7)	0.8878(5)	−0.0932(7)	0.042(1)	4.2(7)
N(8)	0.8343(4)	0.1910(6)	0.285(1)	2.6(6)
N(9)	0.8326(4)	0.2764(6)	0.491(1)	2.8(6)
C(1)	0.6725(5)	0.0714(8)	0.136(1)	2.8(8)
C(2)	0.7210(4)	0.0728(7)	0.148(1)	2.3(7)
C(3)	0.7190(5)	0.1949(7)	0.078(1)	2.7(7)
C(4)	0.6712(5)	0.1880(7)	0.065(1)	2.4(7)
C(5)	0.5458(4)	0.1782(7)	0.346(1)	2.0(7)
C(6)	0.5440(5)	0.2197(7)	0.444(1)	2.4(7)
C(7)	0.5881(5)	0.3096(7)	0.356(1)	3.0(7)
C(8)	0.5876(5)	0.2678(8)	0.257(1)	2.8(7)
C(9)	0.4853(5)	0.0635(8)	0.047(1)	2.9(8)
C(10)	0.5458(5)	−0.0100(8)	−0.004(1)	2.7(8)
C(11)	0.8272(5)	−0.0032(8)	0.016(1)	2.8(7)
C(12)	0.8476(6)	−0.0732(8)	−0.002(1)	3.2(8)
C(13)	0.9078(6)	−0.043(1)	0.107(2)	5(1)
C(14)	0.8878(5)	0.0290(8)	0.130(1)	4.0(9)
C(15)	0.8208(5)	0.1625(7)	0.384(1)	2.8(7)
C(16)	0.8199(5)	0.2018(7)	0.485(1)	2.7(7)
C(17)	0.8494(5)	0.3042(7)	0.393(1)	2.9(7)
C(18)	0.8500(5)	0.2635(8)	0.291(1)	3.1(8)

a) Disordered. Refined with multiplicity of 0.5.

Table 3. Selected Bond Distances (Å) and Angles (degree) for $\{[Cu_2(Me_2pz)_{3/2}(Me_2pz)_{3/2}](ClO_4)_2\cdot 2(Me_2CO)\}_\infty$

Atom	Atom	Distance	Atom	Atom	Distance
Cu(1)	N(1)	1.990(9)	Cu(1)	N(3)	1.950(8)
Cu(1)	N(5)	2.002(9)	Cu(2)	N(2)	1.962(8)
Cu(2)	N(4)	2.019(8)	Cu(2)	N(6)	1.978(8)
N(1)	C(1)	1.30(1)	N(1)	C(4)	1.33(1)
C(1)	C(2)	1.41(1)	C(3)	C(4)	1.38(1)
C(2)	C(5)	1.46(2)	C(3)	C(6)	1.48(2)
N(2)	C(2)	1.33(1)	N(2)	C(3)	1.36(1)
N(3)	C(7)	1.35(1)	N(3)	C(10)	1.34(1)
C(7)	C(8)	1.39(1)	C(9)	C(10)	1.37(1)
C(7)	C(11)	1.46(2)	C(10)	C(12)	1.48(2)
N(4)	C(8)	1.36(1)	N(4)	C(9)	1.34(1)
N(5)	C(13)	1.31(1)	N(5)	C(16)	1.33(1)
C(13)	C(14)	1.40(1)	C(15)	C(16)	1.38(1)
C(14)	C(17)	1.50(1)	C(15)	C(18)	1.50(2)
N(6)	C(14)	1.36(1)	N(6)	C(15)	1.33(1)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
N(1)	Cu(1)	N(3)	128.9(4)	N(1)	Cu(1)	N(5)	106.0(4)
N(3)	Cu(1)	N(5)	124.1(3)	N(2)	Cu(2)	N(4′)	118.4(3)
N(2)	Cu(2)	N(6′)	130.2(3)	N(4′)	Cu(2)	N(6′)	111.4(3)
Cu(1)	N(1)	C(1)	125.2(8)	Cu(1)	N(1)	C(4)	117.6(8)
Cu(2)	N(4′)	C(9′)	122.0(7)	Cu(2)	N(4′)	C(8′)	121.9(7)
Cu(2)	N(2)	C(2)	122.1(7)	Cu(2)	N(2)	C(3)	119.8(7)
Cu(1)	N(5)	C(13)	122.8(8)	Cu(1)	N(5)	C(16)	118.9(7)
Cu(1)	N(3)	C(7)	120.7(7)	Cu(1)	N(3)	C(10)	119.6(7)
Cu(2)	N(6)	C(14)	121.2(7)	Cu(2)	N(6)	C(15)	121.6(7)
C(1)	N(1)	C(4)	117.1(9)	C(2)	N(2)	C(3)	118.2(9)
C(7)	N(3)	C(10)	119.7(9)	C(8)	N(4)	C(9)	116.0(9)
C(13)	N(5)	C(16)	118(1)	C(14)	N(6)	C(15)	117.2(9)

The Cu(1) and Cu(2) atoms are jointed by 2-Clpz molecules so that square planar motifs ($Cu_4(2\text{-}Clpz)_4$) of Cu(1)–N(1)–N(2)–Cu(2)–N(9)–N(8′)–Cu(2′)–N(2′)–N(1′)–Cu(1)–N(3)–N(4) are built as shown in Fig. 2-(b). With sharing the Cu(1)–N(1)–N(2)–Cu(2) edges, the $Cu_4(2\text{-}Clpz)_4$ motifs are linked to afford one-dimensional ribbons, which runs parallel to the orthorhombic *c* axis. Furthermore the residual 2-Clpz molecules (Fig. 2(a) and (b)) joint neighboring ribbons with sharing the Cu(1) atom at the corner, providing two-dimensional pleated sheets on the bc plane. Figure 2(b) also indicates the Cu···Cu distances ranging from 6.818(4) to 6.952(4) Å, longer by 0.2 Å than those of **1**.

Relationship between Structures of Polymer and the Ligands. In this work the factors governing the polymer structures are sought, especially focusing on substituents on the planar pyrazine molecule. Before answering the question how methyl substituents contribute to the polymer structures, we see the influence of methyl groups for pyridine derivatives simpler than pyrazines. In the case of monomeric copper(I) complexes 2-methylpyridine (2-Mepy) affords no four-coordinate but three-coordinate form, which is in good contrast with the four-coordinate complex of non-substituted pyridine.[18,19] This is simply because steric repulsion hinders the four-coordination of the ligand. For one-dimensional copper(I) polymers having CuSCN backbones[20] the similar steric effect of methyl subsituents is found. The polymerization modes are greatly affected by the substituents. Pyridines having methyl groups on 3- and 4-position are identical with non-subsituted pyridine. 3-Mepy and 4-Mepy afford zigzag chains, in which each copper atom is four-coordinate ($Cu(L)_2(SCN)_2$, L=pyridine derivative). One the other hand methyl group on 2-position hinders the second coordination of 2-Mepy itself and instead of 2-Mepy sulfur atom of SCN is co-

Table 4. Bond Distance in Å and Bond Angles in Deg for $\{[\mathrm{Cu_2(2\text{-}Clpz)_{4.5}}](\mathrm{ClO_4})_2\}_\infty$

Atom	Atom	Distance	Atom	Atom	Distance
Cu(1)	N(1)	2.14(1)	Cu(1)	N(3)	2.02(1)
Cu(1)	N(4)	2.13(1)	Cu(1)	N(5)	2.01(1)
Cu(2)	N(2)	2.05(1)	Cu(2)	N(6)	2.05(1)
Cu(2)	N(8)	2.05(1)	Cu(2)	N(9)	2.08(1)
N(1)	C(1)	1.30(2)	N(1)	C(4)	1.31(2)
N(2)	C(2)	1.34(2)	N(2)	C(3)	1.36(2)
N(3)	C(5)	1.33(2)	N(3)	C(8)	1.35(2)
N(4)	C(6)	1.36(2)	N(4)	C(7)	1.32(2)
N(5)	C(9)	1.30(2)	N(5)	C(10)	1.34(2)
N(6)	C(11)	1.31(2)	N(6)	C(14)	1.32(2)
N(7)	C(13)	1.29(2)	N(7)	C(12)	1.31(2)
N(8)	C(18)	1.35(2)	N(8)	C(15)	1.30(2)
N(9)	C(17)	1.32(2)	N(9)	C(16)	1.36(2)
Cl(1)	C(1)	1.73(1)	Cl(2)	C(5)	1.73(1)
Cl(3)	C(9)	1.73(2)	Cl(4)	C(12)	1.73(2)
Cl(5)	C(15)	1.73(1)	C(1)	C(2)	1.39(2)
C(3)	C(4)	1.38(2)	C(5)	C(6′)	1.35(2)
C(7)	C(8′)	1.36(2)	C(9)	C(10′)	1.39(2)
C(11)	C(12)	1.38(2)	C(13)	C(14)	1.41(2)
C(15)	C(16′)	1.36(2)	C(17)	C(18′)	1.38(2)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
N(1)	Cu(1)	N(3)	98.8(4)	N(1)	Cu(1)	N(4)	97.2(4)
N(1)	Cu(1)	N(5)	121.0(5)	N(3)	Cu(1)	N(5)	126.3(5)
N(3)	Cu(1)	N(4)	110.8(4)	N(4)	Cu(1)	N(5)	99.1(4)
N(2)	Cu(2)	N(6)	109.2(4)	N(2)	Cu(2)	N(8)	108.8(4)
N(2)	Cu(2)	N(9)	105.9(4)	N(6)	Cu(2)	N(9)	105.6(5)
N(6)	Cu(2)	N(8)	114.6(4)	N(8)	Cu(2)	N(9)	112.3(5)
Cu(1)	N(1)	C(1)	128(1)	Cu(1)	N(1)	C(4)	115.8(9)
Cu(1)	N(3)	C(5)	128.0(9)	Cu(1)	N(3)	C(8)	120(1)
Cu(1)	N(4)	C(6)	128.0(9)	Cu(1)	N(4)	C(7)	116.6(9)
Cu(1)	N(5)	C(9)	120(1)	Cu(1)	N(5)	C(10)	124(1)
Cu(2)	N(2)	C(2)	125.9(9)	Cu(2)	N(2)	C(3)	117.5(9)
Cu(2)	N(6)	C(11)	122.7(9)	Cu(2)	N(6)	C(14)	120(1)
Cu(2)	N(8)	C(15)	124.6(9)	Cu(2)	N(8)	C(18)	118(1)
Cu(2)	N(9)	C(16)	126(1)	Cu(2)	N(9)	C(17)	118.8(9)

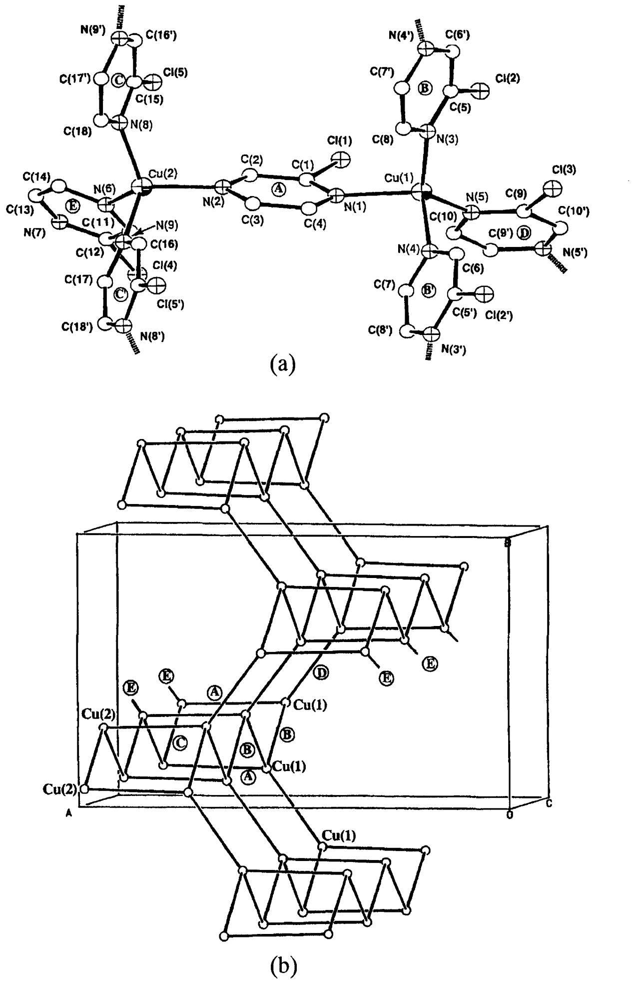

Fig. 2. (a) ORTEP views of portions of $[\mathrm{Cu_2(2\text{-}Clpz)_{4.5}}](\mathrm{ClO_4})_2]_\infty$. (b) Schematic arrays of infinite sheets. Copper atoms and bridging 2-chloropyrazine molecules are denotes by open circles and solid lines, respectively. Each pyrazine ring is distinguished by alphabetical label.

ordinated (Cu(2-Mepy)(SCN)$_2$), providing ribbon type (double chain) backbones. Further addition of a methyl group on 6-position releases a SCN group to give a three-coordinate of each copper, CuL(SCN)$_2$, resulting in zig-zag chains. These findings reveal that methyl groups on pyridine ring primarily influence the copper(I) coordination sphere, which is responsible for polymerization modes.

Figure 3 indicates clearly the role of the pyrazine derivatives in building polymer structures. More than two subsituents on pz ring hinder four coordination, providing infinite zig-zag chains or sheets of the cross-linked chains. Me$_4$pz gives a zig-zag chain, $\{[\mathrm{Cu_2(Me_4pz)_3}](\mathrm{ClO_4})_2\}_\infty$,13) whose motifs are two- and three-coordinate copper atoms ('CuL$_2$' and 'CuL$_3$'). In the case of disubstituted pz the copper geometry is a trigonal-planar, and the zig-zag chains are cross-linked by additional pz molecules to form the sheets having hexagonal motifs. 2,6-Me$_2$pz and 2,3-Me$_2$pz afford the polymers of **1** and $\{[\mathrm{Cu_2(2,3\text{-}Me_2pz)_3}](\mathrm{ClO_4})_2\}_\infty$,14) respectively. Four-coordinate copper units ('CuL$_4$') in two-dimensional sheets are realized by use of 2-Clpz, which is distinct from mononuclear [Cu(2-Mepy)$_3$].18) 2-Clpz molecules are coordinated to copper so that four chlorine atoms meet together very closely. This four-coordination makes the polymer structure quite unique. Although the polymer compounds with 'CuL4' type are not found in non-subsituted pyrazine, we believe that it is possible to get polymer structures as well as 2-Clpz. Great difficulty in crystallization is a main reason to slow down this synthetic and structural studies. Inspection of the structures listed in Fig. 3 exhibits that a basic unit of the polymers is regarded as one-dimensional zig-zag chains and the interchain connection largely depends on the spatial factor of the pyrazine molecules, such as size and direction of the substituents. However, it is difficult to determine how much the subsitutuents affect the polymer structure.

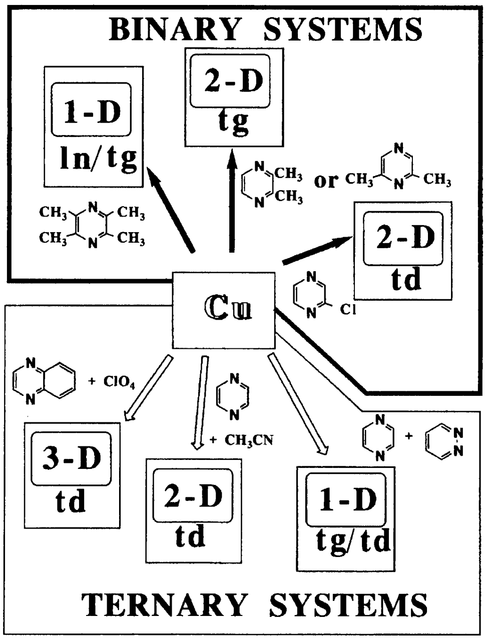

Fig. 3. Formation scheme of polymer structures from various pyrazine derivatives. Abbreviations, ln, tg, and td, indicate linear, trigonal, and tetrahedral geometry of copper, respectively. 1-D, 2-D, and 3-D shows the dimensionality of the polymers.

Usually, the copper geometry is trigonal for binary cationic polymers except for 2-Clpz. Instead of the fourth pz molecules other ligands can be coordinated to the copper to give a four-coordinate geometry. [Cu(pz)(CH_3CN)][13] is an instance of the ternary polymers. The two-dimensional sheets are built by a chair-like Cu_6 units. The large quinoxaline molecules hinders the four coordination and instead of this ligand, an perchlorate ion is weakly bridged to two copper atoms (Cu–O=2.385(8) and 2.536(8) Å), giving three-dimensional polymer structures.[21]

Concerning the synthesis of the infinite polymer structures with 2,6-Me_2pz and 2-Clpz, the following are summarized. First, two-dimensional layers are successfully constituted by use of 2,6-Me_2pz having asymmetric nitrogen donors. Secondly, unique two-dimensional structure is also built by four-coordinate units of Cu(2-Clpz)$_4$, whose coordination is first case in binary copper–pyrazine polymers. Consequently, controlling spatial factors, especially subsitutents on pyrazine, are important factor governing the polymer sturctures such as mode of polymerization and dimensionality. The meaning of this results is that the structure of copper units primarily determine the polymer structure. Thus, the coordination number of copper units is a key in molecular design of copper-pyrazine systems. Pz and its derivatives are relevant for building polymer structures.

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